A proposed new route to d^0 magnetism in semiconductors

J. Berashevich

Thunder Bay Regional Research Institute, 290 Munro St., Thunder Bay, ON, P7B 5E1, Canada and
Max Planck Institute for the Physics of Complex Systems, Nthnitzer Str. 38, 01187 Dresden, Germany

A. Reznik

Thunder Bay Regional Research Institute, 290 Munro St., Thunder Bay, ON, P7B 5E1, Canada and
Department of Physics, Lakehead University, 955 Oliver Road, Thunder Bay, ON, P7B 5E1

Here we propose to induce magnetism in semiconductor utilizing the unique properties of the interstitial defect to act as the magnetic impurity within the α-PbO crystal structure. The Pb_i interstitial generates the p-localized state with two on-site electrons to obey the Hund's rule for their ordering. It is demonstrated that instead of Pb interstitial other non-magnetic impurities of s^2p^x outer shell configuration can be applied to induce d^0 magnetism with possibility to tune the local magnetic moments μ_B by varying a number of electrons $1 \le x \le 3$. The magnetic coupling between such defects is found to be driven by the long-range order interactions that in combination with high defect solubility promises the magnetic percolation to remain above the room temperature.

Spintronics has recently emerged as a widely successful technology that exploits the principles of magnetism, but the classical metal ferromagnets are not applicable there. That has led to the creation of a new branch of research directed at semiconductors exhibiting magnetism at room temperature [1]. The first success in this regard was with the so-called "diluted magnetic semiconductors" created by doping semiconductors with magnetic ions whose inner $3d$ or $4f$ shells being partially filled that allows the ferromagnetic spin alignment [2–5]. A keen interest on ferromagnetic semiconductors also arose when 'non-magnetic' materials were discovered to demonstrate magnetism [6–9]. Origin of so-called d^0 magnetism was proposed to be due to localized sp states: vacancies create a network of unpaired electrons and as interaction between such defects can demonstrate the long-range order, their magnetic coupling occurs [9].

Here we propose to induce d^0 magnetism by forming the interstitial defect Pb_i (Pb_i:$6s^26p^2$ outer shell) within the crystal structure of the tetragonal lead oxide α-PbO. It generates the state occupied by two p-unpaired electrons Pb_i:$6p^2$. Ordering of the localized electrons Pb_i:$6p^2$ obeys the first Hund's rule thus resulting in formation of the stable local magnetic moment of 2.0 μ_B. The spin-polarization energy of such state is $E_M = E_{AFM} - E_{FM}$=0.235 eV, where E_{AFM} and E_{FM} are the total energies of the anti-(AFM) and ferromagnetic states (FM), respectively [10]. Therefore, otherwise than magnetism occurs due to the partially filled p shell instead of the $3d$ or $4f$ shells, Pb_i works exactly as the magnetic impurity. It demonstrates the high on-site spin stability, its p electrons are localized on impurity site showing a weak perturbation with the host (an interaction with the host occurs through Pb_i:$6s^2$ electrons) and in addition, the interstitial defect is almost non-invasive to the electronic and crystal structures of the host. We have established that any impurity of the $s^2p^{1 \le x \le 3}$ outer shell embedded as the interstitial defect into the α-PbO crystal structure would act as magnetic. The p-shell occupation, $p^{1 \le x \le 3}$, can be used to control

the spin ordering between impurities and also to tune the local magnetic moments: $x = 2$ works for 2.0 μ_B, while $x = 1$ or $x = 3$ for 1.0 μ_B. From the technological point of view, the layered crystal structure of α-PbO promises the superior advantages in achievement of the magnetic percolation and more importantly, a practical way for its control: *i)* the crystal structure of PbO type grows in polycrystalline form whose large surface area offers enormous potential for doping (on surface the impurities can be placed on the nearest-neighbours); *ii)* the dopant solubility and long-range order interactions can be manipulated with the impurity atomic radius; *iii)* any compounds of the tetragonal PbO type can be used as a semiconductor matrix.

In our study we applied the generalized gradient approximation (GGA) with the PBE parametrization [11] provided by WIEN2k package for the density functional calculations [12]. The supercell approach (RK_{max}=7) with sufficiently large supercell of 108-atom size ($3\times3\times3$ array of the primitive unit cells) for single impurity and of 160-atom size ($5\times4\times2$) for two interacting impurities have been used. The Pb:$5p, 5d, 6s, 6p$ and O:$2s, 2p$ electrons have been treated as the valence electrons. For integration of the Brillouin-zone, the Monkhorst-Pack scheme using a ($5\times5\times4$) k-mesh was applied. The localization of the impurity wavefunction has been additionally examined with HF applied directly to the unpaired electrons that allows to preserve accuracy provided by DFT but in the same time to correct the unpaired electrons self-interaction [13].

The tetragonal lead oxide α-PbO possesses the layered structure leading to formation of platelets upon compound growth and each platelets is considered as a single crystal. The layers within such crystal are held together by the interlayer interaction of Pb:$6s^2$ electrons [14]. In terms of electronic properties, these interactions induce a deeping of the conduction band at $\mathbf{M}^*$ point [15] and the gap shrinks as interactions enhance. GGA tends to overestimate the interlayer separation in the layered structures but in the same time it also well known to

underestimate the band gap size. For α-PbO system it results in compensation effect [17]: for the lattice parameters optimized with GGA the band gap is only slightly underestimated as 1.8 eV against the experimental value of 1.9 eV [16] (application of the experimental value of the lattice parameters causes the band gap to shrink by 0.22 eV). The correct band gap size is important in investigation of the magnetic impurities: when the band gap size is underestimated the hole-carrying impurity orbital occurs closer to the the host conduction band in turn forcing a delocalization of the defect tails. In order to avoid the spurious long-range order interactions [5] all band structure calculations have been performed for the lattice parameters optimized with GGA. However, since an incorporation of the interstitial becomes easier as interlayer distance increases, the interlayer distance has also crucial impact on the defect formation energy. In order to make correct evaluation of the formation energy, the experimental value of the lattice parameters has been applied for those calculations.

The interstitial defects have never been considered in origin of d^0 magnetism because they do not belong to a class of most common defects in crystalline materials as they induce a significant perturbation of the host lattice resulting in their large formation energy [18]. The layered structure of α-PbO is different, as it allows the foreign atoms to squeeze between layers inducing a minimal lattice deformation to the host immediate neighborhood (see Fig. 1 (a)). As a result, the formation energy of Pb_i is not too high. For the Pb rich conditions/vacuum the neutral charge state is characterized by the formation energy of 1.23 eV (for methods see [17]).

The band diagram and the density of states (DOS) for α-PbO containing Pb_i are presented in Fig. 1 (b) and (c), respectively. The Pb interstitial makes a bond with Pb atom from the host generating the defect state inside the band gap. The defect-induced spin-up and spin-down bands (1^u and 1^d in Fig. 1 (b) and (c)) both show dominant Pb_i:$6p_{x+y}$ character but demonstrate a different behavior. The spin-up band is filled with two electrons and appears just above the midgap at 0.99 eV $+ E_V$, where E_V is a top of the valence band (VB). In contrast, the spin-down band (1^d) is unoccupied and appears at the edge of the conduction band (CB). In order to understand an asymmetry in filling of the spin-up and spin-down states, bonding of Pb_i with the host lattice has to be considered.

The integration of the Pb interstitial into the crystal lattice requires excitation of its ground state $6s^2 6p^2$ to $6s^1 6p^3$. The Pb_i:$6s^1$ and Pb_i:$6p_z^1$ electrons participate in bond formation with the Pb atom from the host which shares its Pb:$6s^2$ electrons (see Fig. 1 (c)). The bonding orbital appears inside VB, while the antibonding forms the CB bottom (see 2^u and 2^d bands and notations of 'bonding' and 'antibonding' at B and C panels to DOS). The length of the Pb_i-Pb bond is fairly short, 2.9 Å, that is indicative of a double bond formation. An out-of-plane displacement of 0.54 Å occurs for the Pb atom involved
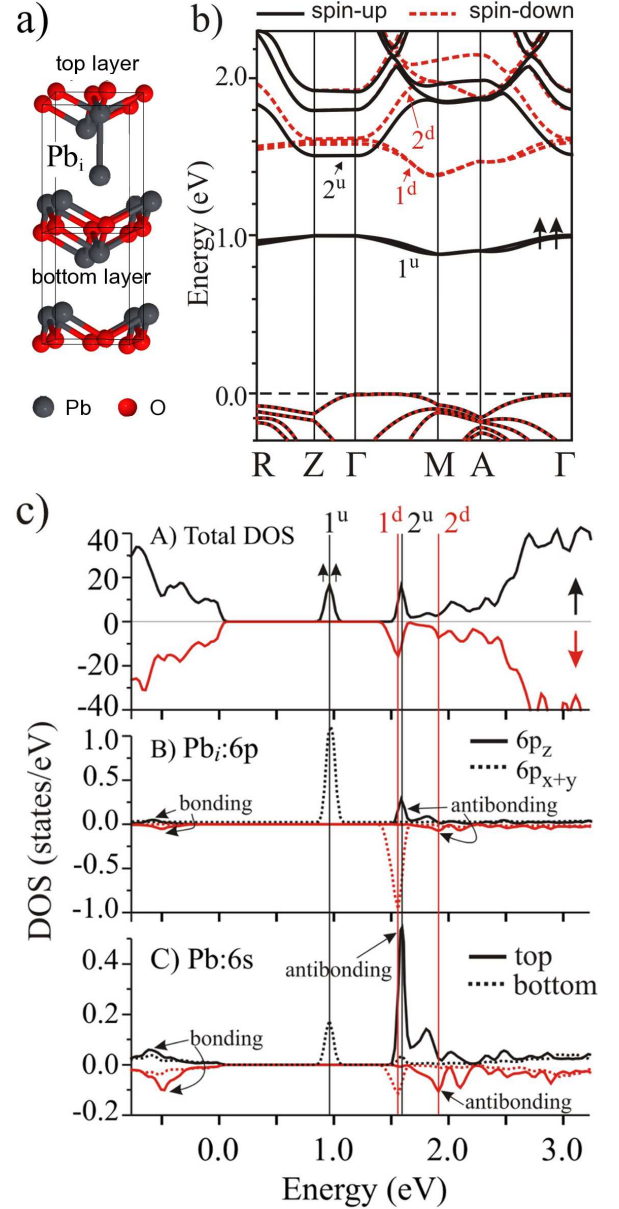

FIG. 1: (a) The Pb interstitial in the layered crystal structure of α-PbO (b) Band diagram: 1^u and 1^d are for the defect induced bands, while 2^u and 2^d are the antibonding orbitals of the Pb_i-Pb bond. (c) Total and partial density of states for Pb_i and host Pb atoms ('top' is referred to Pb atom forming the Pb_i-Pb bond, while 'bottom' for Pb atoms in the bottom layer). The 'bonding' and 'antibonding' in panels B and C are reffered to the Pb_i-Pb bond.

in bonding. Because participation of the host Pb:$6s^2$ orbitals in bonding interferes with interlayer interactions, it alters a behavior of the conduction bands near the CB top: in analogy with the band behavior in a single layer [15], the band deeping at the $\mathbf{M}^*$ point is suppressed.

Therefore, out of three Pb_i:$6p^3$ electrons found in the excited state ($6s^1 6p^3$), only one Pb_i:$6p_z^1$ participates in bonding while the two others Pb_i:$6p_{x+y}$ are left at the

defect site. The Hund's rule dictates both unpaired electrons to occupy the 1^u spin-up band. The empty 1^d spin-down band is pushed up to CB that causes considerably large spin-exchange splitting of order 0.523 eV. The ferromagnetically ordered $Pb_i:6p_{x+y}$ electrons generate the local magnetic moment of 2.0 μ_B. The difference in total energy between the AFM and FM states is found to be $E_M = E_{AFM} - E_{FM}$=0.235 eV thus promising the FM state to be stable well above the room temperature. An application of the HF approach to the unpaired electrons induces further stabilization of the FM state to E_M=0.490 eV due to stronger on-site localization of the impurity wave function (the 1^u orbital is shifted towards the valence band by 0.5 eV thus enhancing the splitting of the 1^u and 1^d orbitals). On the other hand, reduction of the interlayer distance (the experimental lattice parameters are applied) in opposite causes delocalization of the wave function due to stronger hybridization of impurity state with the host lattice.

The $6s^2 6p^2$ electronic configuration is a key point for the Pb interstitial to act as a magnetic impurity: filled s^2 outer shell is required for bonding with the host lattice while partially filled p shell contributes in development of the local magnetic moment. Following this principle, other chemical elements possessing $s^2 p^{1 \leq x \leq 3}$ outer shell can be applied to induce d^0 magnetism. Indeed, several examined impurities have shown a formation of the local magnetic moment, impurity of $x = 1$ or $x = 3$ induces the local magnetic moments of 1 μ_B, while $x = 2$ produces 2 μ_B. The stability of the spin-polarized state is observed to grow substantially with reduction of the impurity atomic radius.

Our studies of localization of the electron density at the defect site has revealed a duality in its behavior. Since occupied band 1^u is located deep inside the band gap, the $Pb_i:6p_{x+y}^2$ electrons shows strong localization on the defect site thus allowing to form the stable local magnetic moment of $2\mu_B$ (see Fig. 2 (a)). However, the long defect tails appear as well but due to bonding/hybridization of the $Pb_i:6s^1$ and $Pb_i:6p_z^1$ electrons from the Pb interstitial and Pb:6s and Pb:6p, O:2p electrons from the host (see partial DOS in Fig. 1 (c)). As a result, the electron density around the defect site is spin-polarized showing an anisotropy in its distribution: the defect tails are symmetrically polarized relative to Pb_i thus contributing in stabilization of the ferromagnetic state.

Since extension of the wave function tails to the host lattice seems to be of the long-range order, it is expected to induce effective defect-defect interactions. In this respect we have investigated an interaction of Pb_i with the O vacancy (V_O) which formation is also favored at the Pb-rich/O-poor limit (oxygen deficiency). In its charge neutral state, V_O is occupied by two electrons showing the strong localization at the vacancy site [17]. Since the virtual hopping is allowed between the states formed by Pb_i and V_O, they can work as compensating centers to each other. For the defects appearing at the nearest-neighbour sites, the FM ordering of the localized spins at Pb_i is
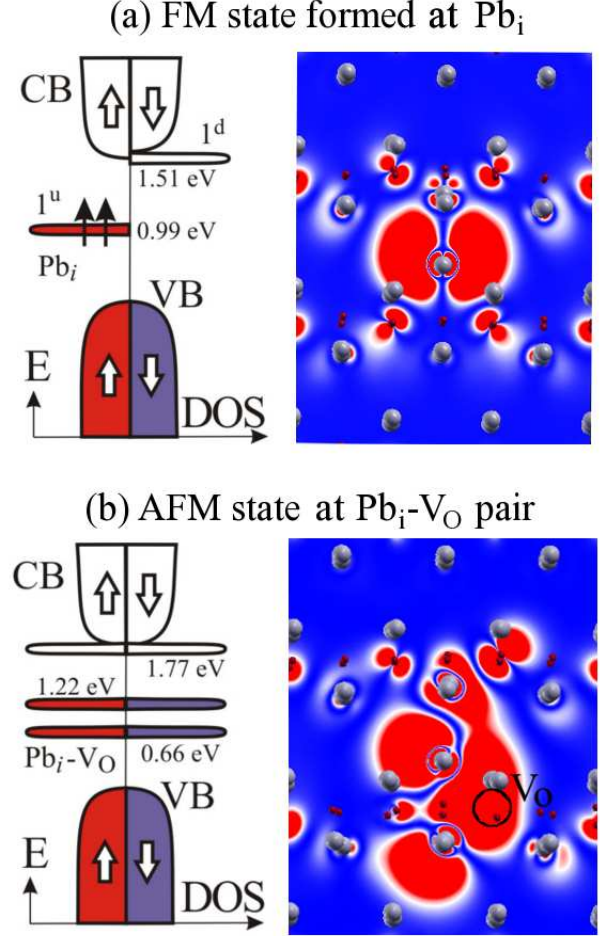

(a) FM state formed at Pb_i

(b) AFM state at Pb_i-V_O pair

FIG. 2: Schematic band diagrams demonstrate a formation of FM (Pb_i) and AFM (Pb_i-V_O pair) states. The energy values are appearance of the defect levels relative to E_V. The electron density map is plotted for isovalues of ± 0.005 e/Å³ with help of Xcrysden. (a) FM state at the Pb_i site. The density map demonstrates the spin density calculated for the energy range (1.0 eV+E_V)$\pm$0.15 eV. (b) An interaction of Pb_i with V_O destroys the FM state at the Pb_i site. The electron density is plotted for the energy range (0.9 eV+E_V)$\pm$0.4 eV.

found to be destroyed due to the strong interaction between defects to be accompanied by hybridization. The $Pb_i:6p_{x+y}$ electrons from the interstitial and the Pb:6s and Pb:6p and O:2p electrons from the host lattice, all have been found to contribute equally in formation of both defect states (see manifestation of the electron density in the inter-defect region in Fig. 2(b)). The strong interactions between defects contribute in lowering of the formation energy of defect pair by 0.84 eV in comparison to the non-interacting defects. With defect separation the electronic interactions are suppressed leading to recovery of the FM state: for distance of 6.2 Å between the defects the local magnetic moment is 1.8 μ_B. However, because interaction of Pb_i with V_O do not vanish completely, the magnitude of the spin polarization energy is

found to be considerably low $E_M = E_{AFM} - E_{FM}$=0.06 eV. Therefore, the electronic interactions between Pb_i and V_O demonstrate the long-range order due to the long tails of the Pb_i interstitial.

For two interacting interstitial defects, as both defects contribute with their tails into the long-range order interactions, the magnetic coupling between them is expected to sustain over the larger distance. The $6p_{x+y}^2$ state is exactly half filled and, therefore, for two interacting impurities the virtual hopping is allowed only in the AFM state making it the ground state [5]. For two Pb interstitials placed on distance 4.1 Å we found that E_M=-0.96 eV while for distance 12.5 Å it drops down to -0.0056 eV. For the C interstitial the interactions are lower as E_M=-0.38 eV for distance 4.1 Å and E_M=-0.0023 eV for 12.5 Å. An application of HF for the localized electrons suppresses E_M almost twice. The AFM interaction between impurities can be switched to FM for the impurity of p^1 occupation of outer shell (for example, In or Ga work for FM state) or for p^2 occupation by choosing the charged state (1+).

In terms of the formation energies of the interstitials, it drastically drops down as the atomic radius decreases. Thus, if the formation energy of the Pb interstitial is 1.23 eV for the Pb-rich/vacuum conditions, it is reduced almost to zero for Ge, Si impurities and already turns to be negative for the C and O impurity (the formation energy of the O interstital is -0.26 eV) thus implying the higher solubility limit with prospects of spontaneous defect appearance. Therefore, it is found that suppression in the magnetic coupling between impurities to occur with reduction of its atomic radius is compensated by simultaneous shift of the impurity solubility limit to the higher defect concentration. For defects appearing on surface, the defect concentration can reach a number of sites available for doping ($\sim 10^{22}\ cm^{-3}$) as the formation energy is reduced further down (for example for the Pb interstitial it drops down by ~ 1.0 eV such as the solubility limit is $10^{20}\ cm^{-3}$).

In summary, we propose to induce the p local orbital magnetism by doping of α-PbO semiconductor with the non-magnetic impurities to appear in layered structure of α-PbO as the interstitial defects. To create conditions for partially filled p shell to act as $3d$ or $4f$ shells of the magnetic ions, i.e. obeying the Hund's rule for the on-site ordering of the unpaired electrons, an impurity of specific $s^2 p^{1 \leq x \leq 3}$ outer shell is required. The combination of the outer shell with the PbO crystal structure is unique because it allows doping to be almost 'non-invasive' to the host lattice and its electronic properties. In particular, bonding between impurity and the host involves only their s^2 outer shell electrons thereby preserving the original electronic configuration of the p shells. In this case, the partially filled $p^{1 \leq x \leq 3}$-shell of impurity generates the localized spins on-site of defect. The main advantage of the defect-induced magnetism over the diluted magnetic semiconductors is duality in its state localization. Thus, the p-localized state formed on site of the Pb interstitial has the localized nature to form the stable local magnetic moment, but impurity-host hybridization results in the extended defect tails. The manifesting long-range order interactions between defects in combination with their high solubility create conditions for magnetic percolation to occur.

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